

Application of an Anthracene Containing Polymer to a Negative Type Photoresist[†]

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Photoresists are very important materials for the photo-fabrication process. They are widely used for the manufacture of microelectronics, printed circuit boards, silk screen printing, optical disks, black matrix of color cathod-ray tubes, and so on. They can be classified into two types on the basis of the solubility changes upon irradiation with UV light, *i.e.*, positive or negative types. The negative type of photoresist is generally more sensitive than the positive one.

It is well known that anthracene or its derivatives dimerize photochemically to give [4+4] cycloadducts across the 9,10-positions of anthracene,¹ and the reaction can be reversed by the shorter wavelength irradiation or by heating.² If the irradiation was carried out in the presence of oxygen, 9,10-endoperoxide as well as photodimer are produced.³ These photochemical reactions of the anthracene groups in the polymer induce considerable changes in their physical properties, for instance, refractive index, absorption, or the degree of solubility etc., which enables them to apply various optoelectronic materials.² Thus, the anthracene containing polymers have been used to develop light-switched chromic devices,^{4,5} electroluminescent devices,⁶⁻⁸ photoresist and channel waveguide applications,⁹ and others.

We are interested in the polymers bearing anthracene (An) groups because of their versatile photoreactivity and various photonic applicabilities. A lots of papers have been reported the application of photochemical [2+2] cycloaddition reactions to photoresist materials. However, as far as we know, the application of [4+4] cycloaddition reactions as a photoresist is very rare.⁹ In this paper, we prepared a homopolymer containing oxyanthracene groups and applied it as a negative type photoresist.

Experimental Section

Materials and instruments. 6-Bromo-1-hexanol and methacrylic anhydride were purchased from Aldrich Chemical Company and used without further purification. Anthraquinone was obtained from Junsei Chemical Company. Anthrone was prepared by the reported procedure.¹⁰ Irradiations were carried out on a Rayonet photochemical reactor (The Southern New England UV Company model 208) equipped

with 365 or 254 nm fluorescent lamps. One module of the photochemical reactor was placed in a horizontal position and irradiated. Light intensity was measured by a Vilber Lourmat radiometer model VLX-3W. An Able model ASS-301 spin coater was used for the preparation of polymer films. Micropatterns were observed by a Zeiss model Axiolab A optical microscope.

Synthesis of 6-(9-anthryloxy)hexane-1-ol (1). A mixture of anthrone (5.00 g, 25.8 mmol), K₂CO₃ (4.30 g, 31 mmol), and 6-bromo-1-hexanol (4.0 ml, 31 mmol) in acetone (30 ml) was refluxed for 48 hours with stirring. The salt formed was removed by filtration from the reaction mixture. After concentration by evaporation of the solvent under reduced pressure, the product was isolated by silica gel column chromatography and purified by crystallization from petroleum ether. The yield and melting point were 35% (2.65 g) and 66-68 °C, respectively.

IR (KBr pellet, cm⁻¹): 3261 (s; -OH), 3051 (s; aromatic C-H), 2935 (s, aliphatic C-H), 1620 (s; anthracene C=C), 1338, 1085 (s; C-O-C), 739. ¹H-NMR (chloroform-d, δ, ppm): 8.29-7.43 (9H, m, anthracene ring), 4.20 (2H, t, An-O-CH₂-), 3.71 (2H, m, -CH₂-OH), 2.08 (2H, m, An-O-CH₂-CH₂-), 1.77-1.55 (6H, m, HO-CH₂-(CH₂)₃-CH₂CH₂-O-An).

C₂₀H₂₂O₂ (294.39) Calc: C 81.63, H 7.48, O 10.88. Found: C 81.67, H 7.43, O 10.90.

Synthesis of 6-(9-anthryloxy)hexyl methacrylate (2). Methacrylic anhydride (0.73 mL, 4.9 mmol) in 5 mL of benzene was added dropwise to a mixture of compound 1 (1.2 g, 4.1 mmol), pyridine (1.32 mL, 8.2 mmol), triethylamine (2.28 mL, 5.2 mmol), hydroquinone (3 mg), and benzene (40 mL), which was refluxed for 3 hours with stirring. After addition of methacrylic anhydride, the reaction mixture was refluxed for 3 days. The reaction mixture was washed with distilled water three times and was dried with MgSO₄. MgSO₄ was removed by filtration, and the filtrate was concentrated by evaporation of the solvent under reduced pressure. A yellow crystalline solid was isolated by silica gel column chromatography. The product was purified by crystallization in petroleum ether. The yield and melting point were 35% (0.52 g) and 32-34 °C, respectively.

IR (KBr pellet, cm⁻¹): 3044 (s; aromatic C-H), 2941 (s; aliphatic C-H), 1724 (s; ester C=O), 1637 (s; anthracene C=C), 1416, 1340, 1088 (s; C-O-C), 740. ¹H-NMR (chloroform-d, δ, ppm): 8.28-7.43 (9H, m, anthracene ring), 6.12, 5.55 (2H, d, CH₂=C), 4.22-4.12 (4H, m, C(=O)-O-CH₂-), and O-CH₂-), 2.07 (2H, m, O-CH₂-CH₂-), 1.95 (3H, s, -CH₃),

[†]This paper is dedicated to Professor Sang Chul Shim of KAIST, who has passed away untimely.

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1.82-1.53 (6H, m, An-O-CH₂-CH₂-(CH₂)₃-).

C₂₄H₂₈O₃ (364.48) Calc: C 79.56, H 7.18, O 13.26. Found: C 79.56, H 7.18, O 13.26.

Preparation of PAn (3). A mixture of compound **2** (1.00 g, 2.76 mmol) and AIBN (9.2 mg, 2 mole%) in THF (5 mL) was purged with N₂ gas for twenty minutes, and the polymerization was carried out at 60 °C for twenty hours. After concentrating the reaction mixture by evaporation of the solvent under reduced pressure, the resulting polymer was purified by double precipitation in methanol (yield 57%).

IR (KBr pellet, cm⁻¹): 3051 (aromatic C-H), 2939 (aliphatic C-H), 1724 (C=O), 1624 (anthracene C=C), 1340 (aromatic C-O), 1261, 1153, 1090. ¹H-NMR (CDCl₃, δ, ppm): 7.2-8.4 (9H, anthracene), 3.8-4.2 (4H, O-CH₂-), 0.8-2.2 (13H, -CH₂-, -CH₃).

Film preparation. A 10 wt% polymer solution was prepared by dissolving PAn (0.1 g) in THF (1 mL), and it was filtered with a Milipore filter. The polymer solution was spin coated on a quartz plate (3.5 × 1.3 cm) by a spin coater with 1000 rpm for 10 seconds at 1st run and 2000 rpm for 10 seconds at 2nd run, respectively. The film on a quartz plate was dried at room temperature for 1 hour followed by drying at 50 °C for 4 hours under vacuum. The film for the pattern formation was prepared on a silicon wafer through the same procedure except spin coating with 1500 rpm on the 1st run for 10 seconds and 3000 rpm on the 2nd run for 10 seconds, respectively.

Measurement.

Dissolved fraction: The two PAn films on the quartz plates, one in an atmosphere of nitrogen and the other in that of air, were irradiated with 350 nm UV light. The irradiated films were dipped in THF (20 mL) for 20 min, and dried at

50 °C for 2 hours under reduced pressure. Dissolved fraction was calculated by the following equation (1) at the isobestic point (322 nm) of the UV absorption spectra;

$$\text{Dissolved fraction (\%)} = -\frac{A_d}{A_i} \times 100 \quad (1)$$

where, A_i is an absorbance of the PAn film at 322 nm upon irradiation with 350 nm UV light and A_d is that at 322 nm after dipping in THF.

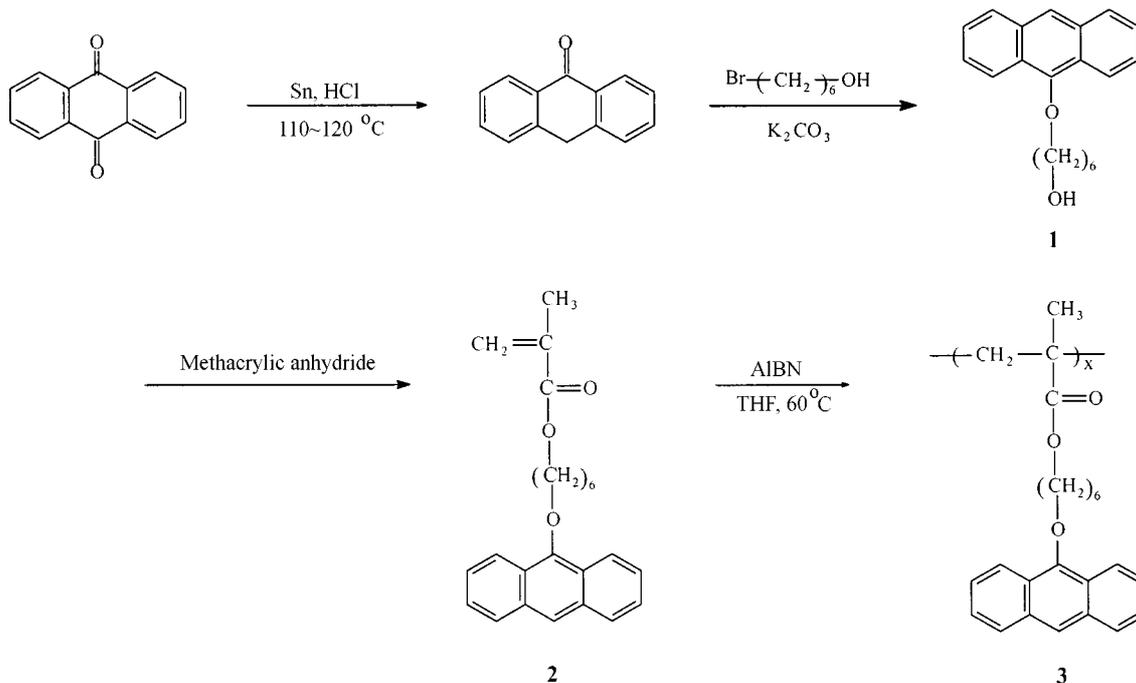
UV absorption spectral changes: Two PAn films on the quartz plate were prepared. One in an atmosphere of N₂ and the other in an atmosphere of air were placed under the UV lamp and irradiated. UV absorption spectral changes upon irradiation with 350 nm UV light (light intensity; 1.6 mW/cm²) were observed.

Pattern formation. A PAn film on the silicon wafer was covered with a photomask and irradiated with 350 nm UV light for 20 min. The irradiated film was dipped in 40 mL of THF for 20 seconds followed by drying at 50 °C for 2 hours. The micropattern formed on the silicon wafer was observed by an optical microscope.

Results and Discussion

Recently, Schopov *et al.*¹¹ reported the preparation of compound **1**, a new monomer containing anthracene group, and studied the photochemical reaction of its methacrylate copolymer. Concomitantly, we¹² have presented a synthetic route for the preparation of compound **1** and its homopolymer in different way.

Scheme 1 shows a synthetic route for the preparation of a monomer and a homopolymer containing anthracene groups. Anthrone was prepared from the reduction of anthraquinone



Scheme 1

with tin. 9-Hydroxyanthracene (9-anthrol) exists mainly anthrone due to the keto-enol tautomerization¹³ and anthrone easily oxidized to anthraquinone. The compound **1**, a blue fluorescent compound, was prepared from the reaction of anthrone with 6-bromohexanol in the presence of K_2CO_3 in acetone.

Generally, methacrylic esters were synthesized from the reaction of methacryloyl chloride with alcohols in the presence of amine. However, anthrone and 9,10-anthraquinone were produced with the product ratio of 1 : 4, when the reaction was run with methacryloyl chloride and compound **1**. This seems to be due to the hydrolysis of the compound **2** by HCl, a side product of the reaction. So, compound **2** was prepared through the reaction of compound **1** with methacrylic anhydride followed by the column chromatography and recrystallization. Compound **2** did not crystallize easily at room temperature due to the low melting point (30-32 °C). Compound **2** has a blue fluorescence.

PAn, a polymer containing anthracene groups was prepared by polymerization of compound **2** in the presence of catalytic amount of AIBN. It is soluble in DMF, DMSO, THF, and chloroform, but insoluble in methanol or ether. PAn has a good film forming property on the solid matrix. The molecular weight (\bar{M}_n) and polydispersity of PAn were 6,300 and 1.94, respectively. The glass transition temperature (T_g) measured by DSC and the thermal decomposition temperature (T_d) measured by TGA were 50.6 and 300 °C, respectively. This indicates that PAn is relatively thermally stable compared with PMMA.

The polymer containing anthracene groups underwent crosslinking through the photodimerization reaction of anthracene groups. This reaction can be applied to a negative type of photoresist.

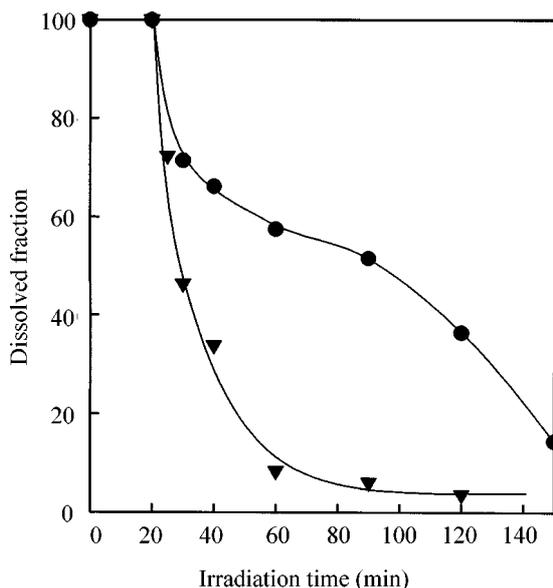


Figure 1. Plot of the dissolved fraction as a function of irradiation time of a PAn film upon irradiation with 350 nm UV light in an atmosphere of air (▼) and N_2 (●). Dipping solvent; THF, dipping time; 20 sec.

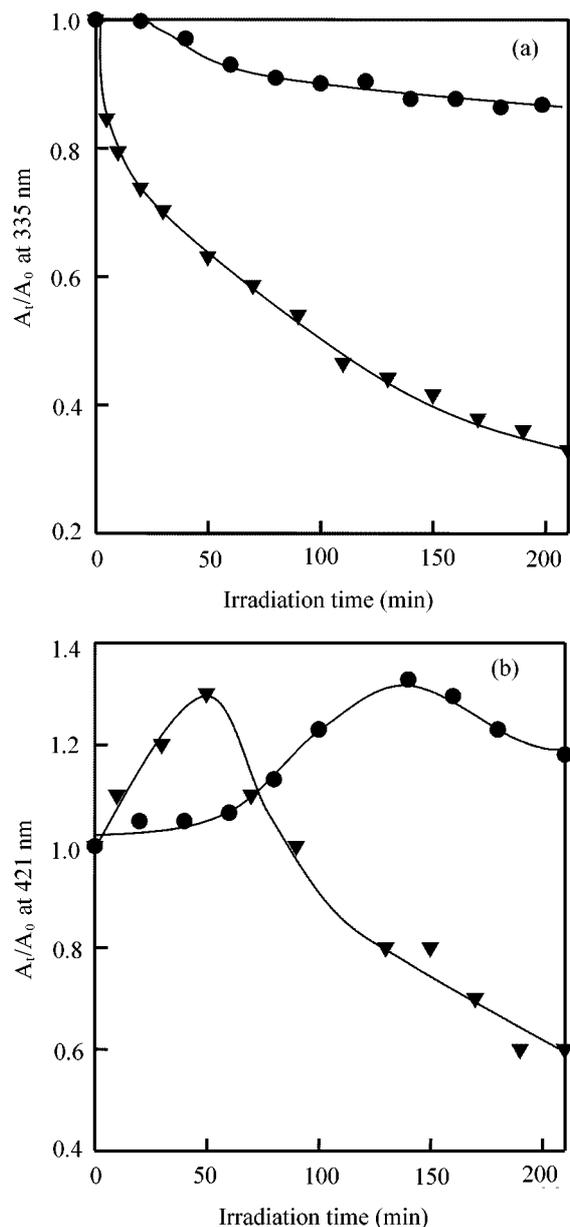


Figure 2. Plots of A_t/A_0 of a PAn film as a function of irradiation time at (a) 335 nm and (b) 421 nm in an atmosphere of N_2 (●) and air (▼), respectively.

The PAn film was soluble in THF or chloroform before irradiation, while it became insoluble after irradiation. Figure 1 shows dissolved fraction of the PAn film in THF as a function of irradiation time. The dissolved fraction decreased upon irradiation with 350 nm UV light as a result of photo-crosslinking. The decrease rate of the dissolved fraction in air is faster than that in N_2 . Thus, the photo-crosslinking in an atmosphere of air is more effective than that in an atmosphere of N_2 . This result indicates that photo-crosslinking of the PAn was induced not only by photodimerization but also by photooxidation reaction.

In order to understand the difference in the photo-crosslinking reaction of PAn in an atmosphere of N_2 or air, its photochemical reaction was studied by the UV absorption

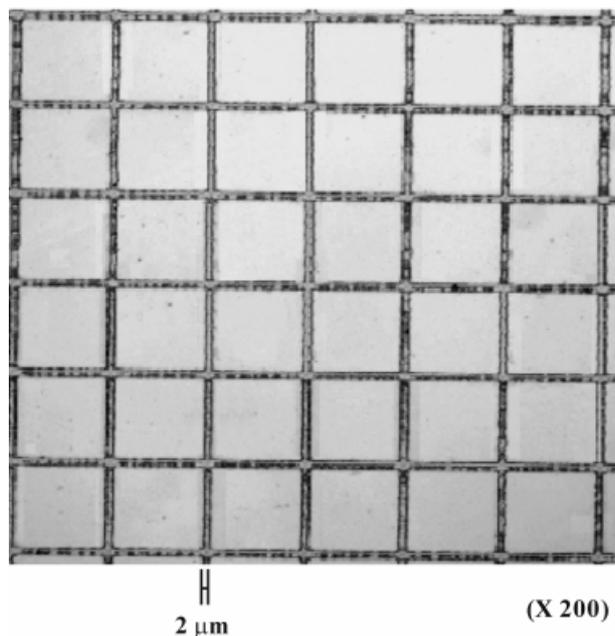


Figure 3. An optical micrograph of a negative micropattern of the PAn film on a silicon wafer after irradiation of 2.1 J/cm² followed by developing in THF for 20 sec.

spectroscopy in the film state. Figure 2 shows the plot of the A_t/A_0 of a PAn film at (a) 335 and (b) 421 nm as a function of irradiation time in an atmosphere of N₂ or air. The relative decrease in absorbance at 335 nm in an atmosphere of N₂ was smaller than that in air. This seems to be due to that the photodimerization of the anthracene groups in the polymer is the only photochemical reaction in the nitrogen atmosphere, while the endoperoxide formation as well as photodimerization took place concomitantly in an atmosphere of air.

It should be noted that the absorption band at around 400~450 nm comes from the anthracene dimer that was produced by the photodimerization of anthracene.¹⁴ As shown in Figure 2(b), the absorbance ratio of the PAn film at 421 nm in an atmosphere of N₂ increased steadily upon irradiation during 130 min. However, in the presence of oxygen, it increased somewhat during the beginning 50 minutes of irradiation time, and then steadily decreased as a result of photooxidation.

The photolysis of anthracene in an atmosphere of N₂ produces the anthracene photodimer as the only product. Irradiation in an atmosphere of air led to the formation of the photodimer as the minor photoproduct and the endoperoxide as the major photoproduct. The endoperoxide underwent thermal decomposition to produce several secondary oxidation products.³ It seems to be very likely that the photo-decomposition products of anthracene endoperoxide groups

in the polymer side chain also induce cross-linking.

Figure 3 shows a texture of a line and space pattern of the PAn film on a silicon wafer. Although the experimental conditions were not fully optimized, the line width of the pattern with 1-2 μm could be obtained. The irradiated part was insoluble in THF, while the unirradiated part was soluble in THF for negative patterning.

In conclusion, we prepared a An monomer **2** in different way comparing with the reported procedure. The homopolymer of **2**, PAn, was soluble in various organic solvents and has a good film forming property on the solid matrix. The rate of decrease in the dissolved fraction of the PAn film in an atmosphere of air was faster than that in an atmosphere of N₂. This seems to be due to the photo-crosslinking of the PAn film, that was induced not only by the photodimerization but also by the photooxidation reaction of the anthracene groups in the polymer side chains. Thus, the PAn behaves a negative type of photoresist. A micropattern with line width of about 1-2 μm could be obtained after developing with THF.

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